



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Emanuel I. Cooper, et al.

Examiner: John P. Sheehan

Serial No: 09/634,171

Art Unit: 1742

Filed: August 9, 2000

Docket:ARC920000067US1(13521)

For: CoFe ALLOY FILM

Dated: December 11, 2003

Commissioner for Patents
P.O. Box 13450
Alexandria, VA 22313-1450

DECLARATION OF EMANUEL I. COOPER UNDER 37 C.F.R. § 1.132

Sir:

I, Emanuel I. Cooper, hereby declare and say that:

(1) I am one of the applicants named in U.S. Application Serial No.

09/634,171, filed with the United States Patent and Trademark Office on August 9, 2000;

(2) I am familiar with the subject matter disclosed in U.S. Application

Serial No. 09/634,171, filed August 9, 2000; and have reviewed the applied reference,

namely the article to E.M. Kakuno, et al., entitled "Structure, Composition, and

Morphology of Electrodeposited $\text{Co}_x\text{Fe}_{1-x}$ Alloys", J. Electrochemical Soc., Vol. 144, No.

9, September 9, 1997 pp. 3222-3226 that was cited in the Office Action dated September

15, 2003;

(3) Additional experiments and data have been carried out to establish that the claimed composition is not obvious relative to the disclosure of Kakuno, et al. cited by the Examiner in the Office Action dated September 15, 2003;

(4) The experiments performed and reported in this Declaration were conducted by Hong Xu, one of the named co-inventors in this case, or they were carried out under her direct supervision or control. Hong Xu and I discussed each experiment prior to performing the same and we discussed the results thereof. We both collaborated on preparing the write-up detailing the experiments preformed herein as well as the results that are obtained therefrom. Hong Xu is presently unavailable to sign this document because she is out on maternity leave;

(5) Specifically, experiments have been performed to show that the cobalt-iron binary alloy electroplated film of the present invention has different properties as compared with the films that are obtained using the procedure disclosed in the Kakuno, et al. disclosure. In this regard, I submit that the properties of electroplated CoFe films are not only related to alloy composition, but are also determined by the electroplating conditions, such as bath chemistry, with or without additives, mixing, current density, pH, temperature and magnetic field.

Besides, magnetic properties, especially magnetic moment, are extremely sensitive to impurity concentrations in the films. All the applicants of the present application have experience with an additive free bath. It is one of the spirits of the present application to invent an innovative way to prevent CoFe from oxidation during plating, and to use a sulfate only bath to prevent the other impurity incorporation such as nitrogen, thus high magnetic moment of at least 2.3 Tesla can be achieved. It is noted that the present application doesn't preclude the presence of some oxygen and iron oxide in the plated CoFe film. However, in order to achieve the magnetic moment of at least

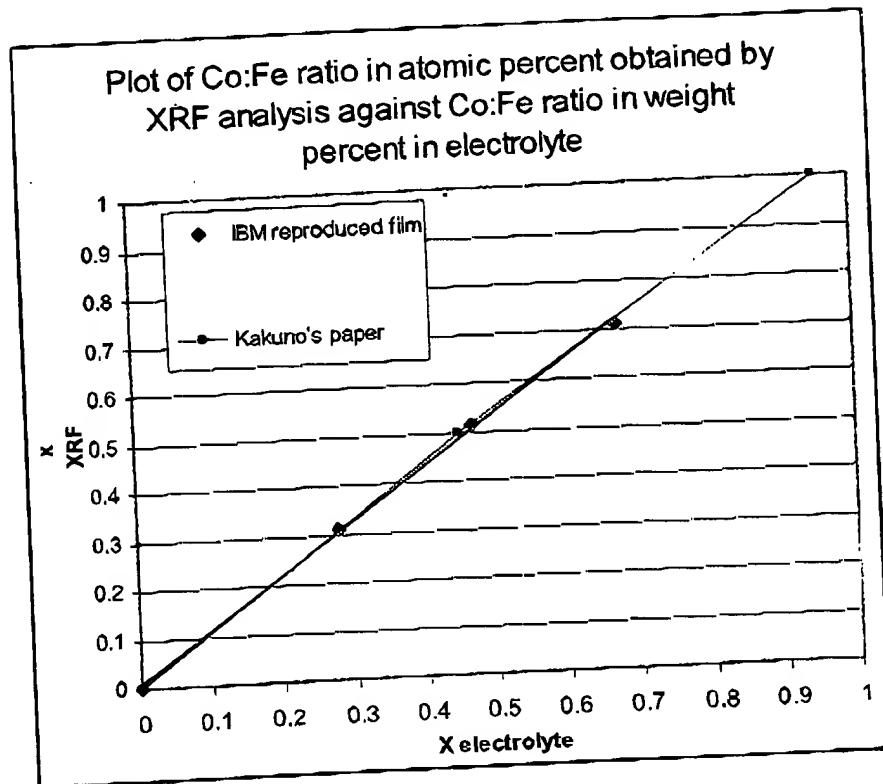
2.3 Tesla, the plated CoFe films have to be substantially free of oxygen and other impurities such as nitrogen.

(6) The purpose of the following experiments aim to reproduce the CoFe films produced using the process disclosed in Kakuno, et al. using the conditions disclosed therein. The follow table provides a description of the experimental set up that was used to form CoFe films provided in the Kakuno, et al. disclosure.

	Kakuno's paper	Reproduced conditions used	Explain the differences
Plating system	Stationary parallel plate; Pt counter electrode; Ag/AgCl reference electrode	Stationary parallel plate; 250 ml solution in beaker Pt counter electrode; Hg/HgSO ₄ reference electrode	In Kakuno, et al., there is no information for the volume of the solution. A 250 ml solution was chosen for convenience. A different reference electrode was used. All potentials are versus Hg/Hg ₂ SO ₄ reference, which is 0.4 V more positive than Ag/AgCl as reported in the paper. So the -1.6 V corresponds to Kakuno, et al. -1.2 V.
Power supply	EG&G PAR potentiostat/galvanostat (Model 273A)	EG & G PAR potentiostat/galvanostat (Model 273A)	

Substrate	(100) textured polycrystalline Cu plates mechanically polished with 1um diamond and then chemically polished. Area of plates: 0.80 cm ² (see Figure 4 in Kakuno's paper for the structure of the substrate)	(100) textured polycrystalline Cu disks mechanically polished with 1um diamond Area of plates: 0.98 cm ² The following graph is the x-ray diffraction data for the Cu substrate and reproduced CoFe films	When one compares the X-ray diffraction data between Kakuno, et al. and XRD data of the present invention, one will find that the Cu disks have the same structure as Kakuno's plates, indicated by the same 2 theta location for the Cu (111) and Cu (002). The intensity of the peak is proportional to metal thickness. The striking difference, as shown by the magnitude of the Co(110) peak, is in the much lower degree of apparent crystallinity in the high-Fe Kakuno compositions (Fe64 and Fe76) as compared to the Fe76 film of the present invention. This means that the grains in the Kakuno films are much smaller and that the relative volume of intergranular space (proportional to intergranular area) is much larger, and/or that the Kakuno films are much less textured, again probably due to intergranular phases interfering with textured crystal growth.
Bath chemistry	Reagent grade Cobalt Sulfate and Iron Ammoniac Sulfate immediately prior to each experiment; x molar of metallic cobalt and $0.7-x$ molar of metallic iron.	Reagent grade Cobalt Sulfate and Iron Ammoniac Sulfate immediately prior to each experiment; x molar of metallic cobalt and $0.7-x$ molar of metallic iron.	We can't dissolve required Cobalt Sulfate and Iron Ammoniac-Sulfate for 1M concentration at room temperature of 21 °C in our lab even overnight. In order to have a freshly prepared bath, 0.7M solution was used for plating. 0.7M concentration is already a highly concentrated solution. Study found that plated film composition is related to the ratio of $\text{Fe}^{2+}/\text{Co}^{2+}$ in the solution, not the absolute solution concentration (See results and discussion section).
Temperature	Room temperature; exact value not reported	Room temperature of 21 °C	
Magnetic field	not mentioned	Not applied	
pH	As prepared, not adjusted; not reported	As prepared, not adjusted; measured pH=3.55	
Potential (V)	-1.0, -1.2, -1.4	-1.2	Since a different reference electrode was used, the potential for the condition shown is after conversion.
Surface quality	Shiny surface	Dark shiny surface	Kakuno, et al. didn't mention whether the film is dark shiny or bright shiny.

(7) Three CoFe samples (with Fe wt% 31.5, 51.7, 71.1, <1micron) were plated in the stationary system using Kakuno, et al. plating conditions. Our study shows that plated CoFe film composition is related to the iron/cobalt ratio in the solution, not the absolute concentration of Fe or Co in the solution. This result agrees with Kakuno, et al. as shown in the following graph.



Since Kakuno's CoFe films were plated in a system without magnetic field, the films show isotropic properties instead of anisotropic properties of the inventive CoFe films. Because of this isotropic behavior, magnetic moment data can't be obtained. (Loops are attached.)

In order to obtain magnetic moment values for Kakuno's CoFe films, two 5" wafers were plated with CoFe films using Kakuno's chemistry in a paddle cell plating

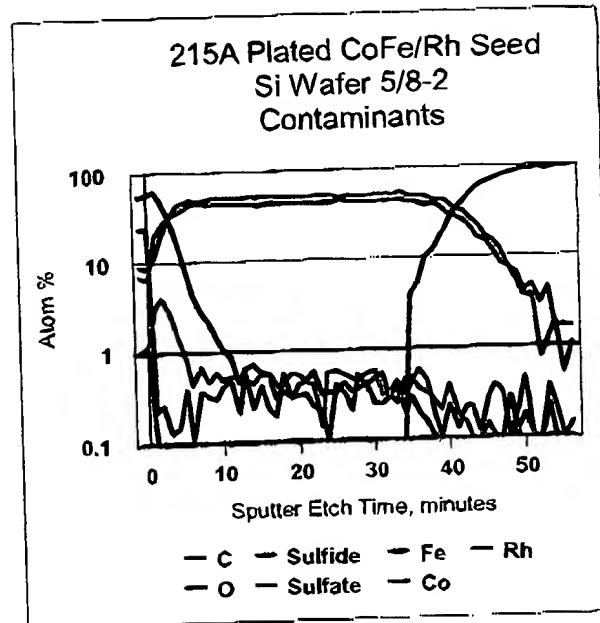
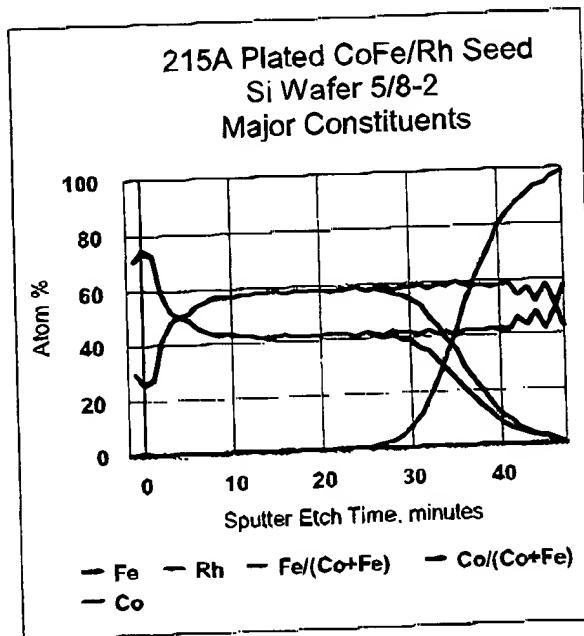
system as indicated in the present application. This system has 800 Oe magnetic field applied perpendicular to the paddle moving direction. Kakuno's plating chemistry, room temperature, pH not adjusted (measured pH=3.55) and current density of 20 mA/cm² were used. CoFe films using Kakuno's plating chemistry show anisotropic behavior, which enables us to measure the magnetic properties. The composition for both films is Fe65wt%. Study shows that Kakuno's films are dark and shiny and are very brittle. After low temperature annealing at 250°C for 8hrs, the film broke completely into small pieces. In contrast, the inventive CoFe films, at this composition, are still intact after annealing. Fig 5 in Kakuno's paper shows cracks in the plated films, confirming this finding. Attached optical photograph for reproduced Kakuno's films also shows such cracks. The magnetic moment for Kakuno's films is 2.2 Tesla compared with 2.4 Tesla for the inventive films at this composition. The resistivity of Kakuno's films at Fe 65wt.% is 44μΩ-cm, while the inventive films at this composition is 38μΩ-cm. The low moment and high resistivity of Kakuno's CoFe films indicate high levels of impurity concentration in the plated films. The finer crystalline grain size and/or the lesser degree of texturing of Kakuno's films as shown by X-ray diffraction, at least for Fe 64wt% and 76wt%, is completely consistent with a higher level of impurities, because of a relatively larger intergranular area occupied by a larger relative volume of impurities that interfere with orderly crystal growth.

Phi Quantum 2000 Electron Spectroscopy for Chemical Analysis (ESCA) was used to analyze the impurity concentration in the plated CoFe films due to its high accuracy in low level impurity analysis. 5" CoFe films were plating in a paddle cell using Kakuno and the inventive bath chemistry and plating conditions, respectively. The

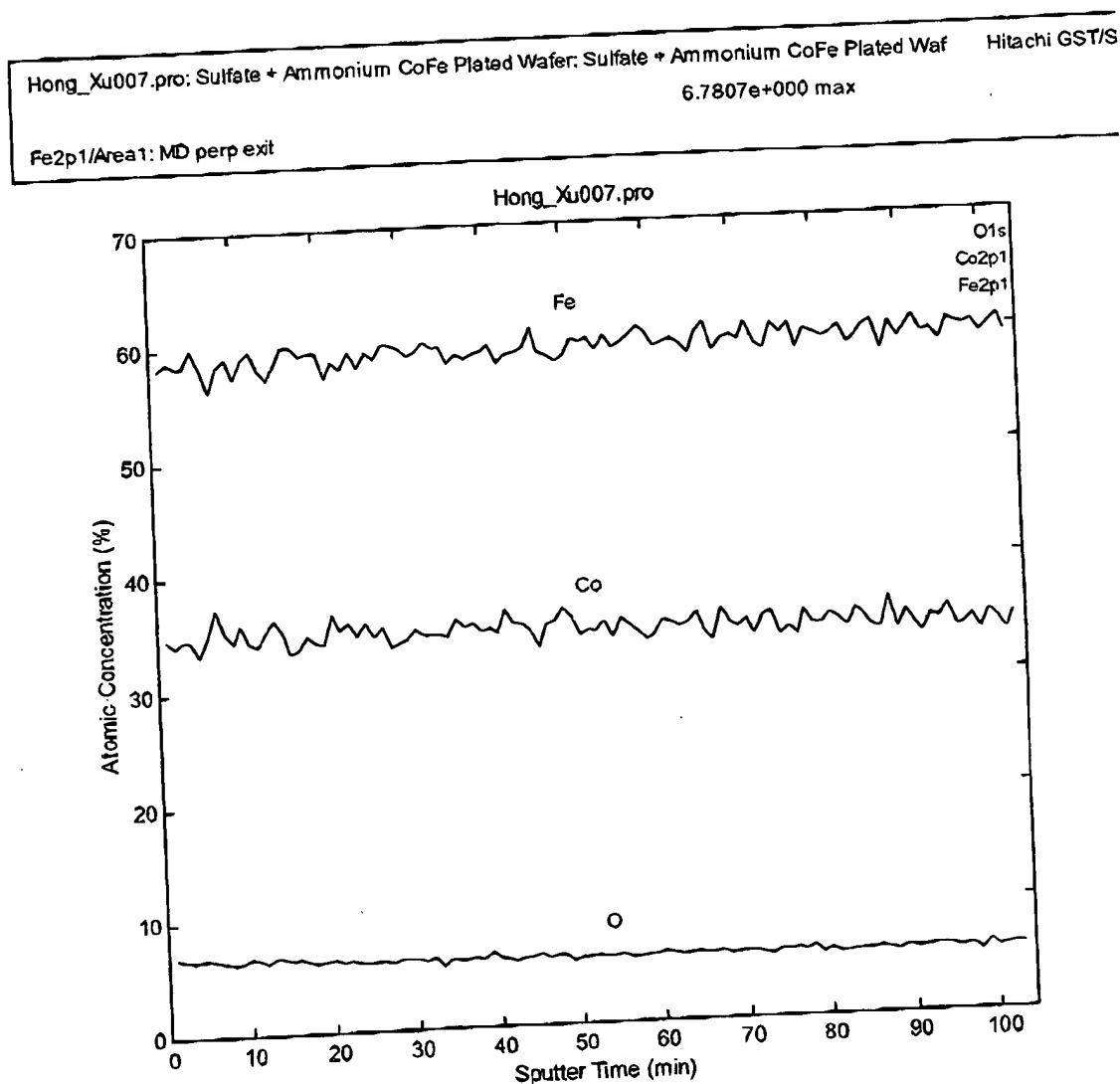
plated film composition is around Fe60 and Co40 for both films. ESCA depth profiles show that Kakuno's film has oxygen content in the bulk as high as 5.7 atom %, while the bulk oxygen content in the inventive film is well below 1 atom %. ESCA data also shows that Kakuno's film has nitrogen content of 0.19 atomic%, while the inventive film is nitrogen free. This is because Kakuno's bath contains Iron Ammoniac Sulfate, while the bath of the present invention has no N-containing constituents.

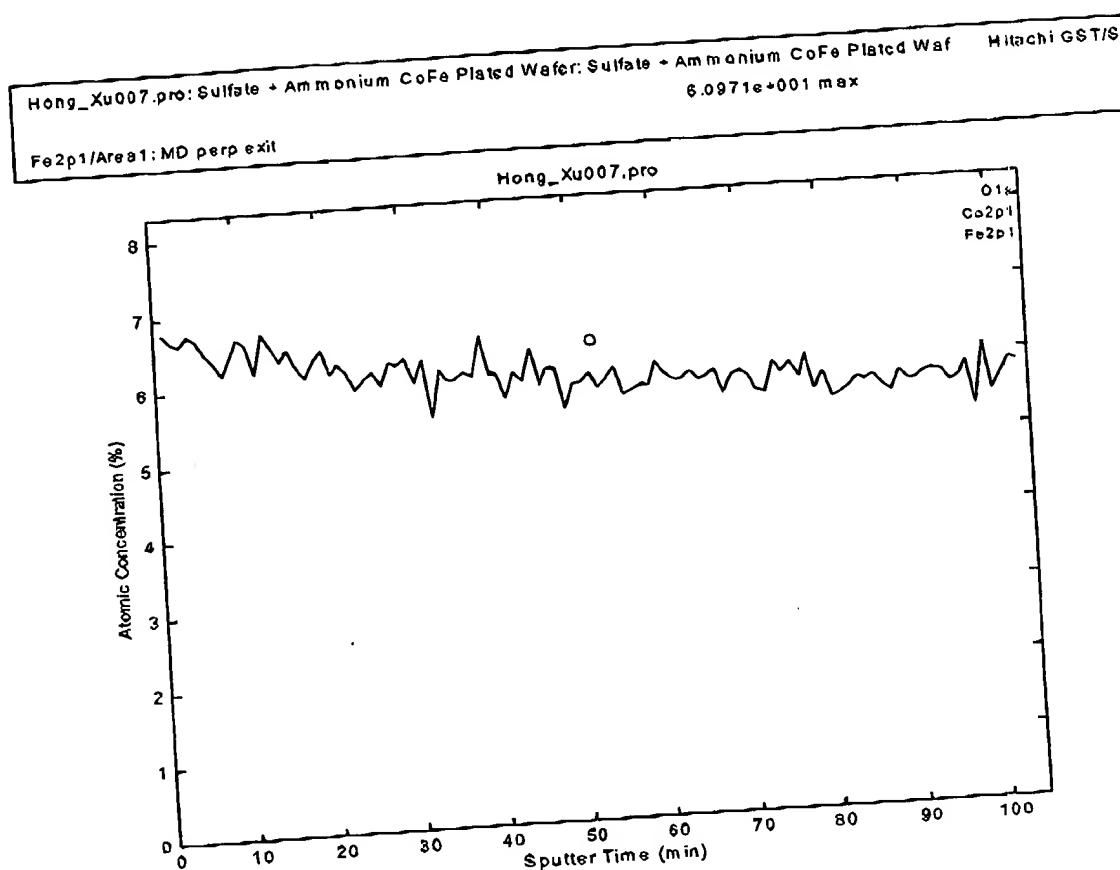
The reason why impurities such as O or N can reduce the magnetic moment is that the bulk magnetic moment is a function of the density of atomic magnetic moments per unit volume. The presence of O and N impurities dilutes the magnetic moment by reducing the volume fraction of the magnetic atoms Fe and Co. Furthermore, oxygen converts a portion of the high-moment Fe and/or Co into low or zero moment oxide compounds such as Fe_2O_3 , Fe_3O_4 , CoFe_2O_4 , FeO or CoO which all have much lower magnetic moment than Fe and Co.

ESCA profile for the inventive film



ESCA profile for Kakuno's film





Species	O	N	Sulfide	Sulfate	Co	Fe
Atom %	5.7	0.19	0.062	0.019	35	59

(8) Summary: Study shows that there are major differences between Kakuno's CoFe films and the inventive films. Kakuno's film has lower magnetic moment of 2.2 Tesla and higher resistance compared with the inventive films at the same composition. Kakuno's films show much less crystallinity in X-ray diffraction, i.e., have finer grain size and/or less texturing. Kakuno's films are very brittle and collapsed after

annealing at a relatively low temperature. All these indicate that Kakuno's films have high levels of impurities incorporated to the plated films. ESCA data confirmed that Kakuno's film has high oxygen content, as high as 5.7 atom%, and substantial nitrogen content, 0.19 atom%, while the inventive film has bulk oxygen concentration well below 1 atom% and is nitrogen-free.

Kakuno's electroplating process is a different process from the inventive CoFe plating process. Kakuno used Iron Ammoniac Sulfate bath without any additives, while in the present invention a purely sulfate bath with an additive to prevent the impurity incorporation into the plated films is used. Study shows that although current density in Kakuno's paper is 10-50mA/cm², which overlaps the disclosed 3-40mA/cm², plating bath chemistry is the key to plate a high moment CoFe films with extremely low oxygen and free of nitrogen impurities, which directly affect the plated film properties.

(9) All statements made herein, of my own knowledge, are true, and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that willful false statements and the like so made may be punishable by fine or imprisonment or both, under Section 1001 Title 18 of the U.S. code and that such willful false statements may jeopardize the validity of the application or any patent issuing therefrom.

Dated: 12/12/2003

Emanuel I. Cooper

Emanuel I. Cooper